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A Phenylene-alkylated Thiophene-based Partially Ladder-type Conjugated Polymer

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Ladder π -conjugated polymers are promising materials for a broad range of organic-based device applications,¹ including light-emitting diodes,² thin film transistors,³ and solar cells.⁴ The rigid coplanar structures of such polymers provide resistance to deformation and enhanced π -conjugation, which result in a number of desirable properties, such as intense luminescence, high carrier mobility, and environmental stability. Most studies in this field have focused on poly(*p*-phenylene)-based polymers, including both step ladder-type or fully ladder-type poly(phenylene)s. However, the commercial exploitation of ladder poly(phenylene) homopolymers has been hampered by their intractable nature. Normally, these materials are chemically or electrochemically produced in the form of powder or as a thin and brittle film, respectively. These are generally difficult to dissolve in common organic solvents owing to their rigid ladder structure containing phenyl rings. To improve the solubility of ladder-type polymers, a number of copolymers with soluble heteroaromatic derivatives have been synthesized,⁵ and/or alkyl and alkoxy side groups have been introduced into the rigid ladder main chain.⁶ Incorporation of these substituent groups was found to induce distortions in the ladder chain, reducing the degree of conjugation and increasing the chain flexibility. These partially ladder-type copolymers therefore possess appreciably higher solubility in common organic solvents compared to the whole ladder polymers.^{6,7}

We recently developed new approaches for preparing both ether- and ester-bridged ladder-type poly(phenylene)s that utilize the BBr₃-promoted intramolecular cyclization.⁸ This method provides significant improvements over other previously reported routes for producing ladder polymers because the cyclization is fast and quantitative.

We present herein the synthesis of partially ladder-type

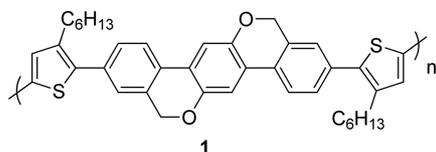


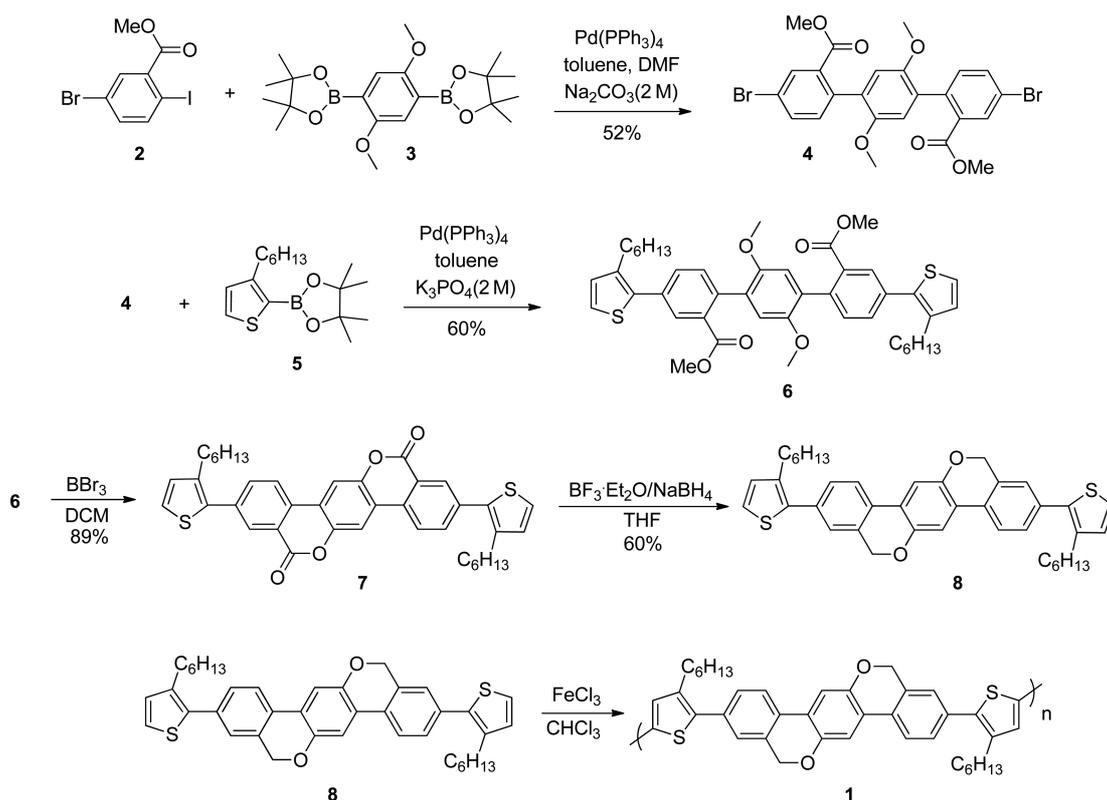
Figure 1. Partially ladder-type phenylene-alkylated thiophene-based polymer **1**.

polymer **1** where the ladder-type planar structure was prepared by the BBr₃-promoted cyclization and an alkylated thiophene was used as a soluble derivative (Figure 1). The photophysical and electrochemical properties of this partially ladder-type phenylene-alkylated thiophene-based conjugated polymer, together with its structural analyses, are also described.

The synthesis of the phenylene-alkylated thiophene-based polymer **1** is described in Scheme 1.⁹ The bis(dibromo dimethoxy diester) (**4**) was prepared by the selective cross-coupling reaction of 5-bromo 2-iodoester **2** with dimethoxy diboronic ester **3**. This was further cross-coupled with 2-hexyl thiophenyl boronic ester **5** under Suzuki conditions to give the precursor of the ladder-type molecule **6**. This was then cyclized by BBr₃-promoted lactonization to afford compound **7**, which was reduced to monomer **8** for further polymerization using sodium borohydride in the presence boron trifluoride-etherate. Finally, iron(III) chloride-mediated oxidative polymerization of **8** led to the desired partially ladder-type phenylene-alkylated thiophene-based conjugated polymer **1**.

Determination of the structure of monomer **8** was carried out using comparative spectroscopic analysis with lactone compound **7**. New signals due to the benzylic proton of compound **8** ($\delta_{\text{H}} = 5.04$) were observed, with a concurrent disappearance of the signal corresponding to the carbonyl group of the lactone ($\delta_{\text{C}} = 160.3$). Single crystals, grown by slow evaporation of a solution of **8** in a mixture of chloroform and hexane, were analyzed by X-ray diffraction in order to verify the planar structure.^{10,11} The results of this analysis confirmed that the molecular structure of compound **8** was the expected partially planar structure with a slight distortion, and the X-ray crystal packing demonstrated that it was arranged by co-facial π -stacking motifs (Figure 2). A well-ordered structure along the *a* axis was also observed in the crystal packing.

Phenylene-alkylated thiophene-based polymer **1** was readily soluble in most organic solvents, including THF and CHCl₃, and had molecular weight (M_w) of 25.2 kDa, as determined by GPC. TGA analysis of polymer **1** displayed



Scheme 1. Synthesis of polymer 1.

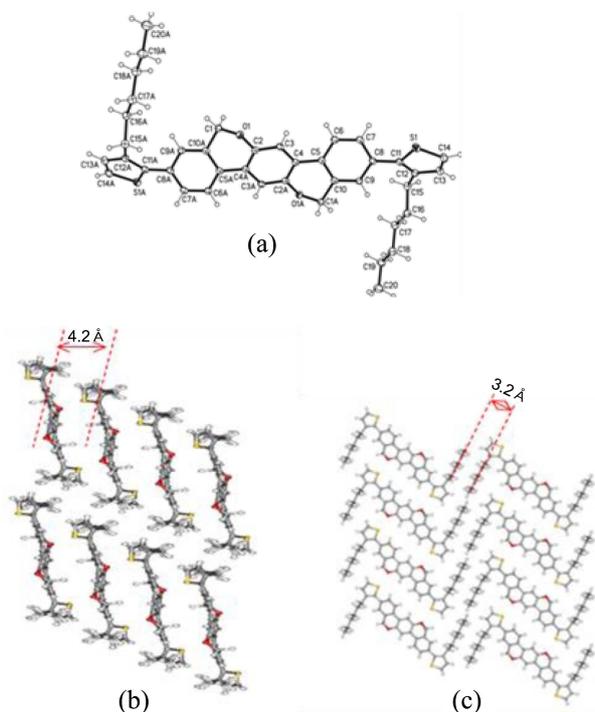


Figure 2. Molecular Structure of 8 along the atom numbering scheme (a) and the packing diagram viewing down the a axis (b,c).

thermal stability up to 310 °C, after which temperature it started to degrade. No characteristic thermal transition was observed by DSC in the temperature range between 20 °C

and 310 °C, indicating that a structural ordering may not occur by thermal annealing.

Polymer 1 was further investigated for its electronic properties using UV-Vis absorption and emission spectroscopies both in solution and as a solid film (Figure 3 and Table 1). The absorption maximum λ_{max} , can be observed at 395 nm for the chloroform solution, and a red shift by 10 nm is evident in the spectrum of the film, indicating a well-ordered crystalline structure of the polymer in its solid state. This was further verified by the emission spectra, where the spectrum of the film showed a red shift by 10 nm. An optical band gap of 2.5 eV was calculated from the onset absorption (500 nm) of the polymer film. This relatively narrow band gap indicates efficient delocalization of π electrons, which was attributed to extended π -conjugation and the planar structure of the partially ladder-type polymer.

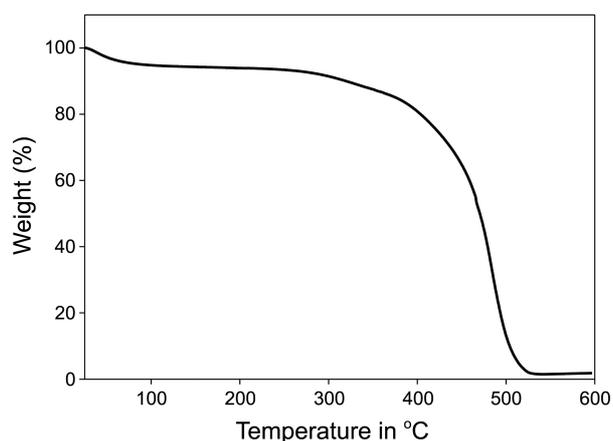
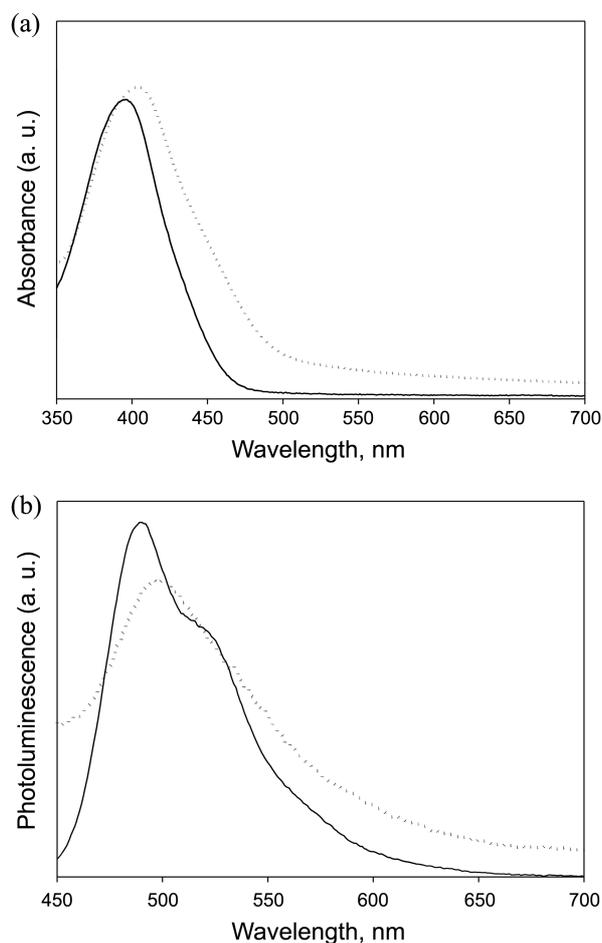
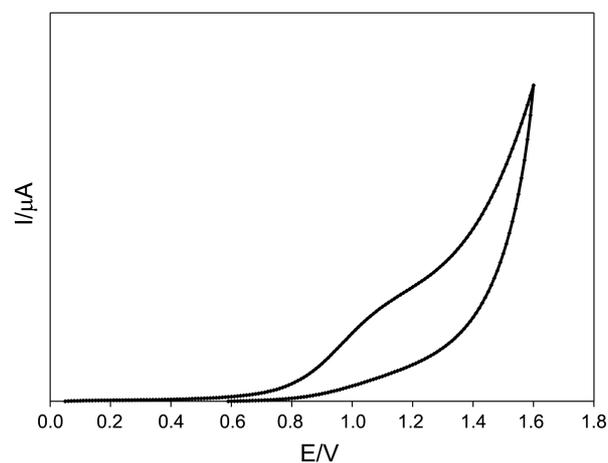
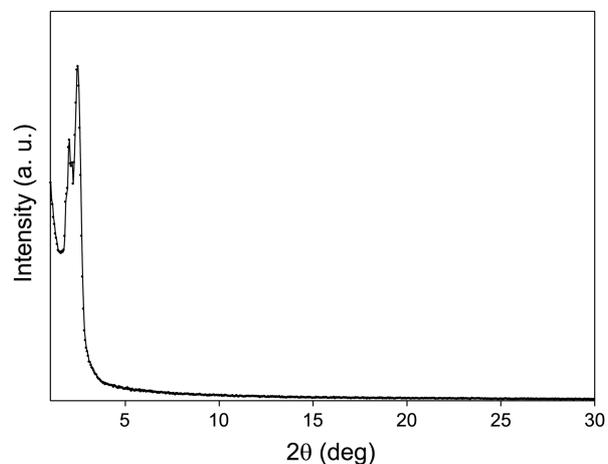
The electrochemical redox behavior of polymer 1 in the cast thin film state was characterized using cyclic voltammetry (CV). The oxidation and reduction cyclic voltammograms of 1 are shown in Figure 4, and the data are summarized in Table 1.

The highest occupied molecular orbital (HOMO) level (ionization potential) was calculated from the first oxidation onset via $E_{\text{HOMO}} = (E_{\text{ox-onset}}(\text{vs Ag/AgCl}) - E_{\text{ox}}(\text{Fc/Fc}^+ \text{ vs Ag/AgCl}))$.¹² The estimated HOMO energy level of polymer 1 was -5.23 eV, and the lowest unoccupied molecular orbital (LUMO) level (electron affinity) was estimated by subtraction of the band gap energy (E_g) from the HOMO level following $E_{\text{LUMO}} = E_{\text{HOMO}} - E_g$, and was calculated as -2.75 eV. These

Table 1. Optical and electrochemical properties of the polymer **1**

Oligomer	UV-Vis absorption spectra			Emission spectra		CV	
	Solution ^a λ_{\max} (nm)	Film λ_{\max} (nm)	$E_g^{\text{opt } b}$ (eV)	Solution ^a λ_{\max} (nm)	Film λ_{\max} (nm)	HOMO (eV)	LUMO (eV)
1	395	405	2.5	490	500	-5.23	-2.75

^aSolution: in chloroform. ^b E_g^{opt} : optical bandgap estimated from the band edge (λ_{onset}) of the absorption spectra

**Figure 3.** TGA thermograms of polymer **1**.**Figure 4.** UV-Vis (a) and emission (b) spectra of polymer **1** in chloroform solution (solid line) and thin film (dotted line).**Figure 5.** Cyclic voltammograms of a film of polymer **1** coated on ITO electrodes measured in acetonitrile containing 0.1 M tetrabutylammonium phosphate at a scan rate of 50 mV/s at room temperature.**Figure 6.** XRD pattern of a thin film of **1** (10 mg/mL in chloroform) drop coated on an OTS modified silicon wafer. The d -spacing was calculated using Bragg's equation, $n\lambda = 2d\sin\theta$.

values suggest that polymer **1** could be a useful material for use in a hole-transporting semiconducting device.

In addition, low angle X-ray diffraction (XRD) analysis was used to estimate the crystalline nature of polymer **1**. The XRD pattern of a thin film of **1**, formed by drop coating onto an octadecyltrichlorosilane (OTS) modified silicon wafer, shows a sharp first order (1,0,0) reflection peak at $2\theta = 2.5^\circ$, with the corresponding d -spacing calculated by Bragg's equation to be 29 Å (Figure 5). Since this d -spacing corresponds to the distance between the polymer main chains in a

lamellar packing structure, the result suggests the presence of a crystalline and well-ordered lamellar organization of the polymer in its solid state. However, in this case, the d-spacing was rather high for efficient intermolecular charge transport.

In conclusion, a partially ladder-type polymer was synthesized, where the ladder-type planar structure was prepared using BBr_3 -promoted cyclization and alkylated thiophene was used as a soluble derivative. The relatively small band gap and broad absorption band, in addition to the crystallinity, make this polymer an attractive material for use in a variety of optoelectronic applications.

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- See Supporting Information for details.
- X-ray crystallographic analysis: The crystal of **8** was attached to glass fibers and mounted on a Bruker SMART diffractometer equipped with graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation, operating at 50 kV and 30 mA, and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. All data collections were performed at 298 K. The data collection 2 θ ranges for **8** is 4.00-57.00. The first 50 frames were retaken after complete data collection and compared. The crystal showed no significant decay and no corrections were applied for the decay. The raw data were processed to give structure factors using the SAINT program.¹³ The structure was solved by direction methods and refined by full matrix least squares against F^2 for all data using SHELXTL software (version 5.10).¹⁴ All non-hydrogen atoms in compound **8** were anisotropically refined. All hydrogen atoms were placed in idealized positions and refined using a riding model. The crystal system in compound **8** belongs to the monoclinic and $P2_1/c$ space group. Crystallographic data in CIF format for the structure reported here have been deposited at the Cambridge Crystallographic Data Centre (Deposition No. **CCDC 931874**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].
- The crystal data, together with the refined atomic coordinates and anisotropic thermal parameters, for **8** and experimental procedures for the syntheses of all compounds are available in the Supporting Information.
- Ferrocenium/ferrocene (Fc^+/Fc) redox couple with a potential of 4.80 eV relative to vacuum as the reference potential was used.
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